

Critical Review of Mercury Chemistry

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Objectives of the Review Were To:

- **Summarize the current “state-of-the-art” of Hg chemistry knowledge in areas important to flue-gas streams from coal-fired boilers**
- **Identify significant gaps in the knowledge**
- **Assess the need for further experimental research to resolve gaps and extend the range of data**

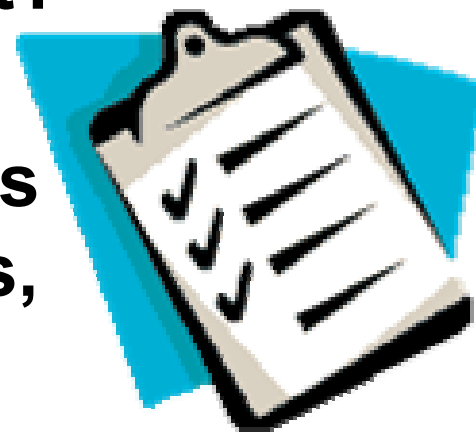


The Review Approach Involved:

- **Identifying the important areas of Hg chemistry for understanding speciation/emissions/control in flue gas from coal-fired boilers**
- **Assembling the most relevant documents publicly available, including journal articles, conference papers, patents, etc.**
- **Critically reviewing the relevant information presented in those documents**

Priorities Were Set by Surveying Mercury Research Experts

- Which reaction types are most important? (e.g., gas-phase, liquid-phase, gas/liquid)
- Which Hg species are most important? (e.g., Hg^0 , HgCl_2 , HgO)
- Which reactants are most important? (e.g., HCl , Cl_2 , SO_2 , NO_2)
- What aspect of reaction chemistry is most important? (e.g., mechanisms, kinetics)



The Survey Respondents Helped Focus the Review

- 62% listed **gas-phase reactions** as most important
- 100% responded that gaseous **Hg⁰** was most important mercury reactant
- **HCl (62%) and Cl₂ (54%)** were the two non-mercury reactants most frequently cited
- 100% said **mechanisms** were the most important aspect of reaction chemistry

Literature Searches Were Conducted Back to 1907



- The earliest relevant paper was in 1949
- Interest in lasers produced several papers in the 70s and 80s on mercury in excited states
- Two of the most important and frequently cited papers were written in '79 and '80
- Renewed interest in the late 80s and early 90s produced several more important papers
- Chemical kinetic models began appearing in the late 90s
- Recent work has added more chemical species and effects of particulate matter

Important Papers Prior to 1989 Included:

- ***Surface Catalyzed Reaction of $\text{Hg} + \text{Cl}_2$, A. K. Medhekar, M. Rokni, D. W. Trainor, and J. H. Jacob, Chem. Phys. Lett., 65 (3), 600-604 (1979); found a fast reaction for Hg^0 with Cl_2 , but attributed this to a surface-catalyzed reaction***
- ***Detection of mercury in air in the presence of chlorine and water vapor, R. Menke and G. Wallis, Am. Ind. Hyg. Assoc. J., 41 (2), 120-124 (1980); found a slow reaction for Hg^0 with Cl_2 ; rate constant calculated from the data in this paper is the one most frequently cited (directly or indirectly) in later work***

Several Important Papers in the Period 1989 – 1992 Included:

- *Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions*, B. Hall, O. Lindqvist, and E. Ljungstrom, *Environ. Sci. Technol.*, 24 (1), 108-111 (1990); **cited 39 times** in ISI's Web of Science; **one of the earliest papers to propose mechanistic conjectures for formation of HgCl_2 in flue gas streams**
- *Chemical Reactions of Mercury in Combustion Flue Gases*, B. Hall, P. Schager, and O. Lindqvist, *Water, Air, and Soil Pollut.*, 56, 3-14 (1991); **cited 51 times; proposed mechanisms for reaction of Hg^0 with both HCl and Cl_2**



Important Papers

1989 – 1992 (cont.):

- ***Reactions Between Mercury Vapor and Chlorine Gas at Occupational Exposure Levels, A. Skare and R. Johansson, Chemosphere, 24 (11), 1633-1644 (1992); cited 5 times; first independent laboratory data that agreed with results of Menke and Wallis, who found a slow homogeneous gas-phase reaction of Hg^0 with Cl_2***

Atmospheric Chemistry Modeling produced these 1991-1998 Papers

- ***Transformation Processes Involving Mercury Species in the Atmosphere - Results from a Literature Survey***, W. H. Schroeder, G. Yarwood, and H. Niki, *Water, Air, and Soil Pollut.*, 56, 653-666 (1991); **cited 69 times; first extensive review of Hg chemistry relevant to atmospheric modeling**
- ***A Chemical Kinetic Mechanism for Atmospheric Inorganic Mercury***, C. Seigneur, J. Wrobel, and E. Constantinou, *Environ. Sci. Technol.*, 28 (9), 1589-1597 (1994); **cited 49 times; first extensive model for the atmospheric chemistry of Hg including gas-phase, liquid-phase, and gas-solid reactions**



Atmospheric Chemistry Modeling 1991-1998 (cont.):

- ***Atmospheric Mercury - An Overview*, W. Schroeder and J. Munthe, *Atmospheric Environment*, 32 (5), 809-822 (1998); cited 97 times; contains 103 references; most recent extensive review of chemical and physical pathways/processes pertinent to Hg in the atmosphere**

In 2000-2001, A Hg/Cl Reaction Mechanism Was Proposed:

- Between 1998 and 2003, a number of mechanisms were proposed by several researchers
- This particular one has been widely accepted and used in later work as part of an overall homogeneous gas-phase Hg oxidation mechanism
 - 1. $\text{Hg}^0 + \text{Cl} + \text{M} \rightleftharpoons \text{HgCl} + \text{M}$
 - 2. $\text{Hg}^0 + \text{Cl}_2 \rightleftharpoons \text{HgCl} + \text{Cl}$
 - 3. $\text{Hg}^0 + \text{HCl} \rightleftharpoons \text{HgCl} + \text{H}$
 - 4. $\text{Hg}^0 + \text{HOCl} \rightleftharpoons \text{HgCl} + \text{OH}$
 - 5. $\text{HgCl} + \text{Cl}_2 \rightleftharpoons \text{HgCl}_2 + \text{Cl}$
 - 6. $\text{HgCl} + \text{Cl} + \text{M} \rightleftharpoons \text{HgCl}_2 + \text{M}$
 - 7. $\text{HgCl} + \text{HCl} \rightleftharpoons \text{HgCl}_2 + \text{H}$
 - 8. $\text{HgCl} + \text{HOCl} \rightleftharpoons \text{HgCl}_2 + \text{OH}$

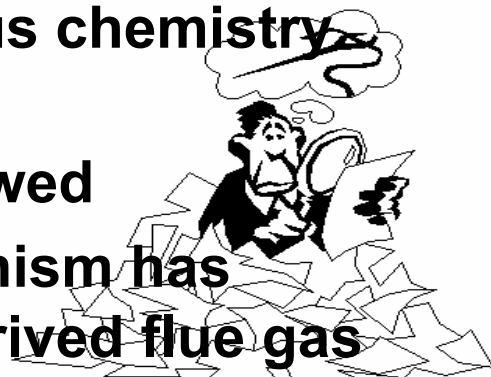
Recent Important Papers Include: (2002-2003)

- *Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Kinetics, Product Studies, and Atmospheric Implications*, P. A. Ariya, A. Khalizov, and A. Gidas, J. Phys. Chem A, 106 (32), 7310-7320 (2002); **new, high-quality laboratory measurements of rate constants gave a significantly lower reaction rate than that of Menke and Wallis**
- *A Mechanism for Mercury Oxidation in Coal-Derived Exhausts*, S. Niksa, N. Fujiwara, Y. Fujita, K. Tomura, H. Moritomi, T. Tuji, and S. Takasu, J. Air & Waste Manage. Assoc., 52, 894-901 (2002); **first model to include gas-solid interactions along with homogeneous gas-phase mechanisms**



Summary

- Review focused on gas-phase homogeneous chemistry of Hg^0 with Cl_2 and HCl
- More than 300 pages of material were reviewed
- A generally accepted eight-reaction mechanism has been developed for Hg oxidation in coal-derived flue gas
- Up to 2002, rate constant for $\text{Hg} + \text{Cl}_2$ reaction was based mainly on 2 papers (Hall, et al., 1991 and Menke, et al., 1980)
- A slow homogeneous reaction was confirmed by Ariya, et al. in 2002 with a rate constant 2 orders of magnitude lower than that derived from Menke and Wallis's data
- Recent modeling points to importance of gas-solid interactions in Hg oxidation



Recommendations

- **Models of Hg oxidation should be checked for revised results using new values obtained for reactions of Hg with both Cl_2 and atomic Cl (from Ariya, et al., 2002)**
- **Other important reactions should be investigated in the laboratory to determine their gas-phase rate constant, such as those for HgCl reacting with either Cl_2 or Cl**
- **Details of the mechanisms for gas-solid interactions should be investigated (e.g., surface reactions, reaction-site characterization)**

Future Work

- **Details of the critical review will be given in a topical report that is in preparation**
- **The review may be extended to include other chemical species and reaction types**
- **Advanced analytical techniques will be used to study gas-solid interactions**



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